



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :  C02F 11/10, C10B 53/00	A1	(11) International Publication Number: WO 00/56671  (43) International Publication Date: 28 September 2000 (28.09.00)
--	----	---

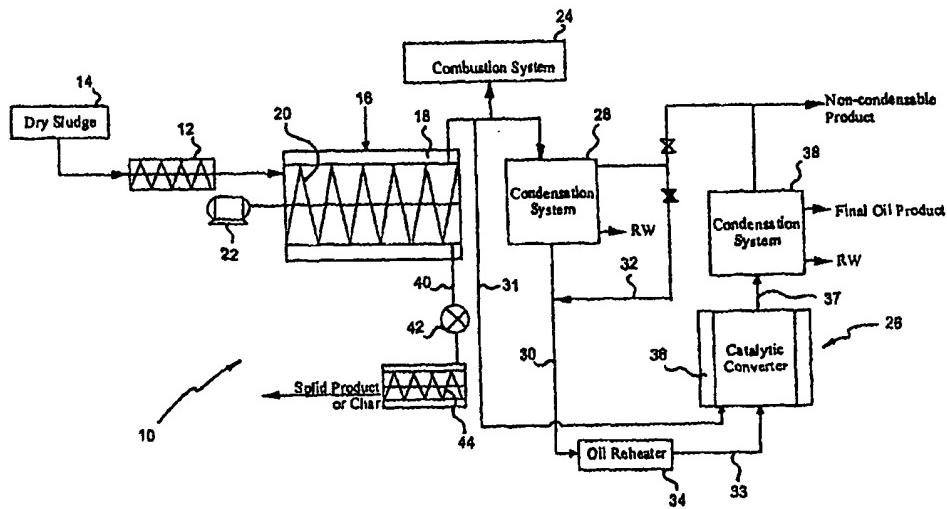
(21) International Application Number: PCT/AU00/00206  
 (22) International Filing Date: 17 March 2000 (17.03.00)  
 (30) Priority Data:  
 PP 9360 22 March 1999 (22.03.99) AU  
 (71) Applicant (for all designated States except US): ENVIRONMENTAL SOLUTIONS INTERNATIONAL LTD. [AU/AU]; 6 Gould Street, Herdsman Business Park, Osborne Park, W.A. 6017 (AU).  
 (72) Inventors; and  
 (75) Inventors/Applicants (for US only): BRIDLE, Trevor, Redvers [AU/AU]; 1B Primrose Street, Perth, W.A. 6000 (AU). SKRYPSKI-MANTELE, Stefan [DE/DE]; Hoffeldstrasse 1, D-77773 Schenkenzell (DE).  
 (74) Agent: WRAY & ASSOCIATES; 239 Adelaide Terrace, Perth, W.A. 6000 (AU).

(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

## Published

With international search report.

## (54) Title: PROCESS AND APPARATUS FOR THE CONVERSION OF CARBONACEOUS MATERIALS



## (57) Abstract

A process for the conversion of sewage sludges, the process characterised by the steps of: (a) feeding dried sludge through a reactor (16); (b) heating the dried sludge in the reactor (16) in the absence of oxygen for the volatilization of oil producing organic materials therein, resulting in gaseous products and sludge residue; (c) transferring the gaseous products from the reactor (16) to a catalytic converter (26); (d) contacting the gaseous products from the reactor (16) or the reheated oil and/or non-condensable products, if any, with a catalyst in the catalytic converter (26) in the absence of oxygen; (e) removing the gaseous products from the catalytic converter (26); and (f) condensing and oil/water separating the gaseous products of the catalytic converter (26).

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

Title

"Process and Apparatus for the Conversion of Carbonaceous Materials"

Field of the Invention

The present invention relates to a process and apparatus for the conversion of  
5 carbonaceous materials. More particularly, the process and apparatus of the  
present invention provides an improvement to the oil product of the conversion of  
the organic components of sewage and industrial sludges.

Discussion of the Prior Art

Sewage sludge is an unavoidable by-product of the treatment of sewage and  
10 other wastewaters. Traditionally, disposal of such sludge is expensive and  
typically constitutes half of the total annual costs of wastewater treatment.  
Historically, the major sludge disposal options have included agricultural  
utilisation, landfilling and incineration. Also historically, wastewater treatment  
plants have been designed to minimise sludge production and most effort is  
15 expended to stabilise and reduce the sludge volume prior to disposal or  
utilisation.

The solids component of sewage sludge comprises a mixture of organic materials  
composed of mostly crude proteins, lipids and carbohydrates. These solids  
further comprise inorganic materials such as silt, grit, clay and lower levels of  
20 heavy metals. For example, a typical raw sewage sludge comprises  
approximately 50 to 90% volatile matter and 25 to 40% organic carbon. Some  
sewage sludges already exceed current land application contaminant standards  
and consequently cannot be used agriculturally or are classified hazardous  
waste, largely due to their organochlorine content.

25 Many sludge processing options have been proposed in the past. Such options  
have the potential to convert a fraction of the organic material into usable energy

- 2 -

and even less have been demonstrated as viable net energy producers at full scale. One common process involves anaerobic digestion of sewage sludge in which approximately 25% of available organic materials is converted to produce a gas rich in methane. Historically, other alternatives have included starved air  
5 incineration and gasification.

A significant problem associated with the above processes relates to the fact that the principle usable energy-containing products are gases which are generally not easily condensable and are of a low net energy content. Accordingly, such gases are impossible or uneconomic to store and must generally be used immediately.  
10 Further, it is generally only practicable to use them to produce relatively low grade energy, such as steam, and flare them to waste during periods of little or no demand. Not surprisingly, it is preferable that any process used result in storable (liquid or solid), transportable and if possible, upgradable energy-containing products. Such products would include synthetic oils. It is consequently  
15 desirable that there be optimum production of storagable energy having any non-storable products, used in the operation of the process itself.

Disposal of sewage sludge has become more problematic recently due to the fact that;

- a) agricultural use of sewage sludge is restricted by its contaminant content,  
20 particularly the organochlorine content, and within this group the dioxins have become the limiting factor,
- b) ocean disposal is banned,
- c) landfilling is to shortly be banned in the European Union; and
- d) incineration of sewage sludge is opposed by the public primarily with respect to  
25 the dioxin issue (reformation of dioxin during hot flue gas cooling). Consequently recent research work on thermal sludge disposal processes concentrates on control of organochlorine compounds across the process.

- 3 -

In US Patents 4618735 and 4781796, there is described a process and apparatus for the conversion of sludges by heating and chemical reaction in order to obtain useful storable products therefrom, including oils. The process comprises the steps of heating dried sludge in a heating zone in the absence of oxygen to a temperature of at least 250°C for the volatilization of oil producing organic material therein, resulting in heating zone gaseous products and sludge residue, removing the said gaseous product from the heating zone; thereafter contacting heated sludge residue in a reaction zone with the removed heating zone gaseous products in the absence of oxygen at a temperature of 280°C to 5 600°C for repeated intimate gas/solid contact at temperatures sufficient to cause gas/solid contact, oil producing reactions to occur within the heating zone, gaseous products catalysed by the heated sludge residue resulting in reaction zone gaseous products containing oil products; removing the reaction zone gaseous products from the reaction zone and separating at least the condensable 10 15 oil products therefrom.

Also disclosed is an apparatus for the conversion of sludge, said apparatus comprising an enclosure establishing a heated heating zone having an inlet thereto for dried sewage sludge and separate outlets therefrom for heating zone gaseous products and residual heating zone solid products; conveyor means 20 within the heating zone enclosure for conveying solid products from its inlet to its solid products outlet; and enclosure establishing a heated reaction zone having separate inlets thereto for gaseous and solid products and separate outlets therefrom for gaseous and solid products; conveyor means within the reaction zone enclosure for conveying solid products from its solid products inlet to its 25 solid products outlet; a heating zone solid products outlet being connected to the reaction zone solid products inlet for the passage of solid products between them; and duct means connecting the heating zone gaseous products outlet to the reaction zone gaseous products inlet.

- 4 -

In US Patents 5847248 and 5865956 there is disclosed a process and apparatus based on the process and apparatus of US Patents 4618735 and 4781796, with the following improvements.

- The gaseous products from the heating zone are transferred to either an indirect or direct condenser with oil/water separation. The resulting oil and/or non-condensable products are injected into a second reactor. Sludge residue or char from the first reactor is transferred to the second reactor by way of a transfer line. The transfer line is equipped with a valve system to ensure that no gaseous products by-pass the condensation system.
- 5
- 10 In the second reactor, provided with heating means, the heated sludge residue from the first reactor is contacted with the revapourised oil or oil and non-condensable gaseous products from the condensation system in the absence of oxygen at a maximum temperature of 550°C. Such allows reductive, heterogenic, catalytic gas/solid phase reactions for the generation of clean
- 15 products and high quality oil product. A conveyor and motor is provided to move the solid product or char through the second reactor.

- Gaseous products are subsequently removed from the second reactor for passage through a further condenser and oil/water separation system or for ducting to a burner for direct combustion. In the case of passage through a
- 20 further condenser and oil/water separation system a volume of non-condensable gaseous product, a volume of reaction water and a volume of refined, low viscosity oil is produced. Solid products or char are removed from the second reactor by way of a further transfer line having provided therein a screw conveyor for ensuring both no air ingress into and no gaseous product egress from the
- 25 second reactor. The screw conveyor is connected to a cooling system to cool the solid product or char to less than 100°C before discharge to atmosphere.

The process and apparatus for the conversion of carbonaceous materials of the present invention has as one object thereof to provide a more simple and cost

effective process and apparatus still able to provide the various advantages of the process and apparatus of US Patents 5847248 and 5865956.

### Disclosure of the Invention

- In accordance with the present invention there is provided a process for the conversion of sewage sludges, the process characterised by the steps of:
- (a) feeding dried sludge through a reactor;
  - (b) heating the dried sludge in the reactor in the absence of oxygen for the volatilization of oil producing organic materials therein, resulting in gaseous products and sludge residue;
  - 10 (c) transferring the gaseous products from the reactor to a catalytic converter;
  - (d) contacting the gaseous products from the reactor or the reheated oil and/or non-condensable products, if any, with a catalyst in the catalytic converter in the absence of oxygen;
  - 15 (e) removing the gaseous products from the catalytic converter; and
  - (f) condensing and oil/water separating the gaseous products of the catalytic converter.

Preferably, sludge residue from the reactor is transferred to a storage bin through a valve system for ensuring both no air ingress into and no gaseous product egress from the reactor.

Still preferably, the feeding of the dried sludge through the reactor utilises a feed system that ensures both no air ingress into, and no escape of gaseous products from, the reactor.

The temperature of the reactor is preferably at least 250°C. The temperature of the reactor is still preferably about 450°C.

The process of the present invention may be further characterised by the method steps of:

- 6 -

- (g) transferring the gaseous products from the reactor to a condensation system to condense the oil product from the gaseous products; and
- 5 (h) reheating water free oil and/or non-condensable products, if any, from the condensation system in an oil re heater.

The condensation system of step (f) preferably comprises a direct condenser. The condensation of step (g) preferably comprises indirect condensation at >100°C.

10 The direct transfer of gaseous products of step (b) from the reactor to the catalytic converter preferably takes place in heat traced lines.

The temperature of the catalytic converter is preferably up to 650°C, thereby promoting reductive, catalytic gas/solid phase reactions and substantially eliminating hetero-atoms, including nitrogen, oxygen, sulphur, and halogens. The catalytic converter temperature is preferably in the range of 400 to 550°C. Still 15 preferably, the catalytic converter temperature is in the range of 400 to 420°C.

The catalytic converter may contain a catalyst, the catalyst being chosen from any of zeolite, activated alumina,  $\gamma$ -aluminium oxide, silicon oxide and oxides of alkali, earth alkali and transition metals. Preferably, the catalyst is zeolite.

20 The process of the present invention may be still further characterised by the step of testing the miscibility of the oil product with a hydrocarbon solvent, for example diesel fuel. In response, the catalytic converter conditions may be modified, thereby optimizing the catalytic conversion of sewage sludge, particularly the elimination of hetero-atoms such as halogens, nitrogen, oxygen and sulphur.

25 In accordance with the present invention there is further provided a process for the optimisation of the process for the conversion of sewage sludges as set out above with particular relevance to the removal of hetero-atoms to produce a

- 7 -

product miscible with a hydrocarbon solvent such as diesel fuel. Oils miscible in a hydrocarbon solvent have lower viscosity, water content and hetero-atom content, i.e. a higher oil quality. Consequently the miscibility with a hydrocarbon solvent can be used as an analytical tool to optimize the process.

- 5 The present invention still further provides a process for the conversion of sewage sludges, the process characterised by the steps of:
  - (a) feeding dried sludge through a first reactor;
  - (b) heating the dried sludge in the first reactor in the absence of oxygen for the volatilization of oil producing organic materials therein, resulting in gaseous products and sludge residue;
  - (c) transferring gaseous products from the first reactor to a first condensation system;
  - (d) transferring sludge residue to a second reactor where it is heated with oil and/or non-condensable products from the first condensation system;
  - (e) transferring the gaseous products of the second reactor to a catalytic converter;
  - (f) removing the gaseous products from the catalytic converter; and
  - (g) condensing and oil/water separating the gaseous products of the catalytic converter.
- 15
- 20

Preferably, the temperature of both reactors is about 450°C. Still preferably, the catalytic converter has a temperature of about 400 to 420°C.

- In accordance with the present invention there is still further provided an apparatus for the conversion of carbonaceous materials, the apparatus characterised by a feed system for dried material to be conveyed, a reactor, and a catalytic converter, the reactor having a solid product discharge outlet and a transfer line provided for transport of gaseous product directly or indirectly to the catalytic converter.
- 25

- 8 -

Preferably, a first condensation system is provided in-line between the reactor and catalytic converter. The first condensation system preferably includes an oil/water separation system.

The catalytic converter is preferably adapted to contact heated catalyst contained  
5 therein with oil or oil and non-condensable products of the condensation system,  
wherein gaseous products may be removed from the catalytic converter. A  
reheater may be provided between the first condensation system and the catalytic  
converter.

A second condensation system is preferably provided to receive gaseous product  
10 from the catalytic converter.

#### Description of the Drawings

The present invention will now be described, by way of example only, with  
reference to two embodiments thereof and the accompanying drawings, in which:

15 Figure 1 is a schematic diagram of an apparatus for the conversion of  
carbonaceous materials in accordance with a first embodiment of the  
present invention; and

Figure 2 is a schematic diagram of an apparatus for the conversion of  
carbonaceous materials in accordance with a second embodiment of the  
present invention.

#### Best Mode(s) for Carrying Out the Invention

In Figure 1 there is shown an apparatus 10 for the conversion of sludges in  
accordance with a first embodiment of the present invention. The apparatus  
comprises a feed system 12 for dried sludge 14. The feed system 12 feeding  
said sludge 14 to a reactor 16. The feed system 12 is such that it ensures both  
25 no air ingress and no gaseous egress from the reactor 16.

The reactor 16 is provided with heating means 18 thereabout, such that dried sludge may be heated therein in the absence of oxygen to at least 250°C. This results in the volatilization of oil producing organic materials in the reactor 16. Further, this reaction provides gaseous products and sludge residue or char.

5 screw conveyor 20 and a motor 22, or their equivalent, is provided to move the sludge through the reactor 16.

- The gaseous products from the reactor 16 are either transferred to a combustion system 24, to a catalytic converter 26 or to a first condensation system 28 with oil/water separation. Further, the first condensation system 28 may comprise
- 10 either a direct or an indirect condenser. The resulting oil is injected, via line 30, with or without any non-condensable products, via line 32, from the first condensation system 28 into an oil re heater 34 where the oil and/or non-condensable products 32 are heated in the absence of oxygen to a maximum temperature of 650°C.
- 15 The gaseous products from the reactor 16 or the preheated oil and/or non-condensable products from the oil re heater 34 are injected into the catalytic converter 26, via lines 31 and 33 respectively. Line 31 from the reactor 16 to the catalytic converter 26 is heat traced. The catalytic converter 26 is provided with a heating means 36 thereabout such that the preheated oil and/or non-condensable
- 20 products may be heated therein in the absence of oxygen to a maximum temperature of 650°C. This allows reductive, catalytic removal of hetero-atoms to produce an oil product of a viscosity that is lower than that of diesel. The refined gaseous products from the catalytic converter 26 are transferred, via line 37, to a final or second condensation system 38 with oil/water separation.
- 25 The solid product or char of the reactor 16 is removed from the reactor 16 by way of a transfer line 40. The transfer line 40 is equipped with a valve system 42 and a screw conveyer (not shown). The valve system 42 is such that it ensures both no air ingress and no gaseous egress from the reactor 16. The screw conveyer is

- 10 -

connected to a cooling system 44 to cool the solid products or char to less than 100°C.

In Figure 2 there is shown an apparatus 100 for the conversion of sludges in accordance with a second embodiment of the present invention. The apparatus

- 5 100 is substantially similar to the apparatus 10 and like numerals denote like parts.

A second reactor 102 is provided to receive the solid product or char of the "first" reactor 16 by way of transfer line 40 and the fluid tight valve system 42. The second reactor 102 is provided with heating means 104 thereabout.

- 10 Revaporphised oil or oil and non-condensable gaseous products from the condensation system 28 are contacted with the char in the second reactor 102 and are heated in the absence of oxygen at a maximum temperature of 550°C. A screw conveyor 106 and motor 108, or their equivalent, are provided to move the solid product or char through the second reactor 102.
- 15 The solid products or char are removed from the second reactor 102 by way of a further transfer line 110 having provided therein a screw conveyor 112 for ensuring both no air ingress into and no gaseous product egress from the second reactor 102. The screw conveyor 112 is connected to a cooling system 114 to cool the solid product or char to <100°C before discharge to atmosphere.
- 20 Gaseous products of the second reactor 102 are removed for injection to the catalytic converter 26 via line 33.

The present invention may be further described with reference to the following example.

Example

The sewage sludge employed in the determination of process data using the continuous apparatus of the present invention was raw sludge from two locations, being the Subiaco Waste Water Treatment Plant (WWTP), Perth, Western Australia, and the Atlanta WWTP, Georgia, United States of America. The sludges were dried to approximately 95% dryness in a drying oven at 70°C prior to processing.

The sludges were processed in either the apparatus 10 or the apparatus 100 as described hereinabove.

- 10 The first series of tests were conducted to demonstrate the impact of the catalytic converter on oil quality. Results are shown in Table 1.

Table 1 - Oil Quality Data: Impact of Catalytic Conversion

Parameter	Run No.	Run 1	Run 2	Run 3	Run 4
Viscosity @ 40°C [cSt]		25.8	29.8	3.2	7.7
Water Content [%]		9.4	6.7	0.72	2.2

- Run 1: Subiaco sludge was processed as described in US patent 5847248.
- 15 As such, gaseous products are condensed after the first reactor and the oil product is injected into the second reactor. Both reactors were operated at 450°C, with the feedrate being 600g/hr. No catalyst was used.
- Run 2: Conversion of raw sludge from the Atlanta WWTP, otherwise as per
- 20 Run 1.

- 12 -

- Run 3: Subiaco sludge processed in accordance with the second embodiment of the present invention with gaseous products being condensed and the oil product, after passing through the reheater prior to the second reactor before being contacted with the catalyst (aluminium oxide impregnated with transition metal oxides) in the catalytic converter.
- 5 The catalytic converter temperature was maintained at 400°C.
- Run 4: As per Run 3 but using Atlanta sludge, with gaseous products being directly transferred to the catalytic converter.

The above results clearly show that the oil viscosity and water content are  
10 reduced significantly by the use of the catalytic converter, for example compare Runs 1 and 3, and 2 and 5.

A second series of tests was conducted to determine the influence of catalyst support. Test results are shown in Table 2.

Table 2: Oil Quality versus Catalyst Support

Parameter	Run No.	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
Viscosity @ 40°C [cSt]		20.9	21.4	7.8	4.7	4.8	27.8
Water Content [%]		1.1	4.4	1.7	1.5	-	4.6

15

- Run 6: Atlanta sludge was processed in accordance with the second embodiment of the present invention, with gaseous products being condensed and the oil product being preheated prior to injection into the second reactor from where it is transferred to the catalytic converter. The temperature of both reactors and catalytic converter
- 20

- 13 -

was controlled at 450°C. Sludge feed rate was controlled at 600 g/hr. Pure Al<sub>2</sub>O<sub>3</sub> was used as a catalyst and was activated at 600°C.

- Run 7: As per Run 6, with Al<sub>2</sub>O<sub>3</sub> being activated at 1200°C as a catalyst.
- Run 8: As per Run 6, with Al<sub>2</sub>O<sub>3</sub> being impregnated with transition metal oxides  
5 and catalytic converter temperature being 400°C.
- Run 9: As per Run 6, using silica gel as catalyst.
- Run 10: As per Run 6, processing Subiaco sludge and using zeolite as catalyst  
with catalytic converter temperature being 420°C.
- Run 11: As per Run 6, using char as catalyst.
- 10 The results show that pure Al<sub>2</sub>O<sub>3</sub> is not as good as Al<sub>2</sub>O<sub>3</sub> doped with transition metals. Silica gel and zeolite appear to be good catalysts and the conversion char is not as good as Al<sub>2</sub>O<sub>3</sub> as a catalyst.

A third series of tests were conducted to assess the impact of catalyst temperature on oil quality and yield. Results are shown in Table 3.

15 Table 3: Oil Quality and Yield versus Catalyst Temperature

Parameter	Run No.	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17	Run 18	Run 19	Run 20
Viscosity @ 40°C [cst]	12.4	8.9	31.7	28.4	26.2	30.3	26.8	16.5	16.4	
Oil Yield [%]	23.3	17.9	25.1	25.3	22.8	22.5	22	21.4	19.6	

- 14 -

- Run 12: Subiaco sludge was processed in accordance with the first embodiment of the present invention, with gaseous products being condensed and the oil product being preheated prior to injection into the catalytic converter. The temperature of reactor and catalytic converter was controlled at 450 and 400°C respectively. Sludge feed rate was controlled at 600 g/hr. Zeolite was used as a catalyst.
- 5
- Run 13: As per Run 12, with catalyst temperature being 420°C.
- Run 14: As per Run 12, with gaseous products being directly transferred to the catalyst and a catalyst temperature of 450°C.
- 10 Run 15: As per Run 14, with catalyst temperature being 470°C.
- Run 16: As per Run 14, with catalyst temperature being 500°C.
- Run 17: As per Run 14, with catalyst temperature being 520°C.
- Run 18: As per Run 14, with catalyst temperature being 530°C.
- Run 19: As per Run 14, with catalyst temperature being 540°C.
- 15 Run 20: As per Run 14, with catalyst temperature being 550°C.
- The above results indicate that the optimal temperature for oil quality, when using a zeolite catalyst is 400 to 420°C, with intermediate condensing, and 530-550°C without intermediate condensing. There does appear to be a drop in oil yield when using the zeolite catalyst up to 550°C.
- 20 A fourth series of tests were conducted to asses the impact of catalyst to oil vapor ratio on oil quality. Results are shown in Table 4.

- 15 -

Table 4: Catalyst to oil vapour ratio versus oil Quality and Quantity

Parameter	Run No.	Run 21	Run 22	Run 23
Weight Hourly Space Velocity (WHSV) [hr <sup>-1</sup> ]	2.3	1.1	0.7	
Viscosity @ 40°C [cSt]	13	4.5	4.8	
Water Content [%]	3.6	1.2	1.1	
Oil Yield [%]	23.2	18.8	18.3	

Run 21: Atlanta sludge was processed in accordance with the second embodiment of the present invention, with gaseous products being condensed and the oil product being preheated prior to injection into the second reactor from where it is transferred to the catalytic converter. The temperature of both reactors and the catalytic converter were controlled at 450°C. Sludge feed rate was controlled at 600 g/hr. Aluminium oxide impregnated with transition metal oxides was used as a catalyst and 80 g of catalyst used.

5

10.

Run 22: As per Run 21, with 165 g of catalyst being used.

Run 23: As per Run 21, with 265 g of catalyst being used.

As expected, the results show improved oil quality at lower WHSV (higher catalyst mass), albeit at a reduced oil yield. There does not appear to be any further improvement in oil quality by reducing the WHSV to below 1 hr<sup>-1</sup>.

15

A fifth series of tests was conducted to assess the impact of catalyst regeneration on oil quality. Results are shown in Table 5.

- 16 -

**Table 5: Catalyst Regeneration versus Oil Quality**

Parameter \ Run No.	Run 24	Run 25	Run 26	Run 27	Run 28	Run 29
Viscosity @ 40°C [cSt]	11.8	17.0	14.6	17.5	20.5	20.2
Oil Yield [%]	16.8	20.6	19.7	16.8	17.1	19.2

- Run 24: Subiaco sludge was processed in accordance with the first embodiment of the present invention, with gaseous products being transferred directly to the catalytic converter. The temperature of the reactor and the catalytic converter was controlled at 450 and 550°C respectively. Sludge feed rate was controlled at 600 g/hr. 210 g of native zeolite was used as a catalyst.
- 5 Run 25: As per Run 24, with the catalyst being regenerated on-line for the first time.
- 10 Run 26: As per Run 24, with the catalyst being regenerated on-line for the second time.
- Run 27: As per Run 24., with the catalyst being regenerated on-line for the third time.
- 15 Run 28: As per Run 24, with the catalyst being regenerated on-line for the fourth time.
- Run 29: As per Run 24, with the catalyst being regenerated on-line for the fifth time.

- 17 -

The results show a slight deterioration in catalyst efficacy via on-line regeneration. However, performance appeared to stabilise after 3 or 4 regenerations.

A sixth series of tests were conducted to compare oil yield and quality from the  
5 dual reactor system with intermediate condensation and the single reactor system without intermediate condensation. The results are shown in Table 6.

**Table 6: Oil Quality Data: Impact of Dual versus Single Reactor Systems**

Parameter	Run No.	Run 30	Run 31
Oil Yield [%]		18.8	16.9
Viscosity [cSt]		4.5	7.6

- Run 30 Atlanta WWTP sludge was processed in accordance with the second  
10 embodiment of the present invention, with gaseous products being condensed after the first reactor and the oil product was injected into the second reactor. The temperature of both the reactor and the catalytic converter was controlled at 450°C. Sludge feed rate was controlled at 600 g/hr. Al<sub>2</sub>O<sub>3</sub> was used as the catalyst.
- 15 Run 31: As per Run 30 but rather in accordance with the first embodiment of the present invention, that is without the intermediate condensing of gaseous products or the second reactor.

These results indicate that the presence of the second reactor, and the condensation of gaseous products before injection thereto, does not have a

- 18 -

significant impact upon oil yield and quality, as might otherwise have been expected, when compared with the apparatus 10 utilising the single reactor 16.

A seventh series of tests were conducted to determine the impact of intermediate condensation on oil quality and yield in the single reactor system. Test results  
5 are shown in Table 7.

**Table 7: Oil Data: Impact of Intermediate Condensing**

Parameter	Run No. Runs 13/32	Run 14
Oil Viscosity [cst]	8.9	31.7
Oil Yield (%)	17.9/23.3	25.1

Runs 13/32: Subiaco sludge was processed in accordance with the first embodiment of the present invention, with gaseous products being  
10 condensed and the oil reheated before being injected to the catalytic converter. The temperature of the reactor was maintained at 450°C and the converter at 420°C. The catalyst was zeolite.

- Run 14: As per Run 13/32 with gaseous products being transferred directly to the catalytic converter which as operated at 450°C.
- 15 These results indicated that the intermediate condenser has a significant impact on oil quality. There is however, a significant oil yield penalty when using the intermediate condenser.

An eighth series of tests was conducted to determine the temperature at which the catalytic converter must be operated to achieve acceptable results in a single

- 19 -

reactor system, without intermediate condensation. Test results are shown in Table 8.

**Table 8: Oil Quality Data: Impact of Catalytic Converter Temperature**

Run No.	Run 32	Run 33
Parameter		
Weight of Catalyst [g]	180	210
Catalyst Temperature [ $^{\circ}$ C]	420	550
Oil Yield [%]	23.3	15.7
Viscosity [cSt]	8.9	11.8

5 Run 32 Subiaco sludge was processed in accordance with the first embodiment of the present invention, with gaseous products being condensed after the single reactor prior to injection to the catalytic converter. The temperature of the reactor and the catalytic converter was controlled at 450 $^{\circ}$ C and 420 $^{\circ}$ C. Sludge feed rate was controlled at  
10 600 g/hr. Zeolite was used as the catalyst.

Run 33: As per Run 32 but without the condensing of gaseous products prior to introduction to the catalytic converter, which was operated at 550 $^{\circ}$ C.

These results indicate that the condensing of the gaseous products of the single reactor prior to injection to the catalytic converter provides an improved oil quality  
15 and yield when compared with not having conducted the condensation step, when using zeolite as the catalyst.

- 20 -

These results further indicate that the catalytic converter must be operated at about 130°C higher if it is desired to produce oil of the same quality without intermediate condensation of the gaseous products of the reactor. As seen in Table 8, this produces a significant drop in oil yield.

- 5    The process for the conversion of sewage sludges of the present invention may be optimised with regard to removal of hetero-atoms through use of miscibility with a standard hydrocarbon source such as diesel fuel. It is apparent that the miscibility with diesel fuel is significantly influenced by the presence of hetero-atoms such as oxygen, nitrogen and sulphur. Such hetero-atoms
- 10    particularly oxygen and sulphur and to a lesser degree nitrogen are removed by the catalytic converter generating an oil that is miscible at any ratio with diesel fuel. Accordingly, the miscibility of the oil product is a direct measurement of the quality of the oil. The miscibility can be directly correlated with viscosity, meaning the better mixing the lower the viscosity. As stated in US Patent 5847248,
- 15    viscosity can also be used as an indicator for the destruction rate of organochlorine compounds and consequently, since the heavy metal oxides present in the catalytic converter are the same as in sewage sludge, the dehalogenation of organochlorines will take place in the catalytic converter at a much higher rate than in the second reactor of US Patents 5847248 and
- 20    5865956, and miscibility can also be used as a control tool for organochlorine destruction.

The process and apparatus of the present invention provide reductive, thermal heterogenic catalytic solid/gas phase reactions in order to obtain storable products with unrestricted use.

- 25    Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

CLAIMS

1. A process for the conversion of sewage sludges, the process characterised by the steps of:
  - (a) feeding dried sludge through a reactor;
  - 5 (b) heating the dried sludge in the reactor in the absence of oxygen for the volatilization of oil producing organic materials therein, resulting in gaseous products and sludge residue;
  - (c) transferring the gaseous products from the reactor to a catalytic converter;
  - 10 (d) contacting the gaseous products from the reactor or the reheated oil and/or non-condensable products, if any, with a catalyst in the catalytic converter in the absence of oxygen;
  - (e) removing the gaseous products from the catalytic converter; and
  - (f) condensing and oil/water separating the gaseous products of the catalytic converter.
2. A process according to claim 1, wherein sludge residue from the reactor is transferred to a storage bin through a valve system for ensuring both no air ingress into and no gaseous product egress from the reactor.
3. A process according to claim 1 or 2, wherein the feeding of the dried sludge through the reactor utilises a feed system that ensures both no air ingress into, and no escape of gaseous products from, the reactor.
- 20 4. A process according to claim 2 or 3, wherein the temperature of the reactor is at least 250°C.
5. A process according to claim 4, wherein the temperature of the reactor is about 450°C.

- 22 -

6. A process according to any one of the preceding claims, the process further characterised by the method steps of:

5                 (g) transferring the gaseous products from the reactor to a condensation system to condense the oil product from the gaseous products; and

(h) reheating water free oil and/or non-condensable products, if any, from the condensation system in an oil reheat.

7. A process according to any one of the preceding claims, wherein the condensation system of step (f) comprises a direct condenser.

10                8. A process according to claim 6, wherein the condensation of step (g) comprises indirect condensation at >100°C.

9. A process according to any one of the preceding claims, wherein the direct transfer of gaseous products of step (b) from the reactor to the catalytic converter takes place in heat traced lines.

15                10. A process according to any one of the preceding claims, wherein the temperature of the catalytic converter is up to 650°C, thereby promoting reductive, catalytic gas/solid phase reactions and substantially eliminating hetero-atoms, including nitrogen, oxygen, sulphur, and halogens.

20                11. A process according to claim 10, wherein the catalytic converter temperature is in the range of 400 to 550°C.

12. A process according to claim 10, wherein the catalytic converter temperature is in the range of 400 to 420°C.

13. A process according to any one of the preceding claims, wherein the catalytic converter contains a catalyst, the catalyst being chosen from any

- 23 -

of zeolite, activated alumina,  $\gamma$ -aluminium oxide, silicon oxide and oxides of alkali, earth alkali and transition metals.

14. A process according to claim 13, wherein the catalyst is zeolite.
- 5        15. A process according to any one of claims 6 to 14, wherein the process further comprises the step of testing the miscibility of the oil product with a hydrocarbon solvent and modifying the conditions of the catalytic converter in response thereto.
16. A process according to any one of claims 6 to 15, wherein the oil product of the process is miscible with a hydrocarbon solvent.
- 10        17. A process according to claim 16, wherein the solvent is diesel fuel.
18. A process for the conversion of sewage sludges, the process characterised by the steps of:
  - (a) feeding dried sludge through a first reactor;
  - (b) heating the dried sludge in the first reactor in the absence of oxygen for the volatilization of oil producing organic materials therein, resulting in gaseous products and sludge residue;
  - (c) transferring gaseous products from the first reactor to a first condensation system;
  - (d) transferring sludge residue to a second reactor where it is heated with oil and/or non-condensable products from the first condensation system;
  - (e) transferring the gaseous products of the second reactor to a catalytic converter;
  - (f) removing the gaseous products from the catalytic converter; and
  - (g) condensing and oil/water separating the gaseous products of the catalytic converter.

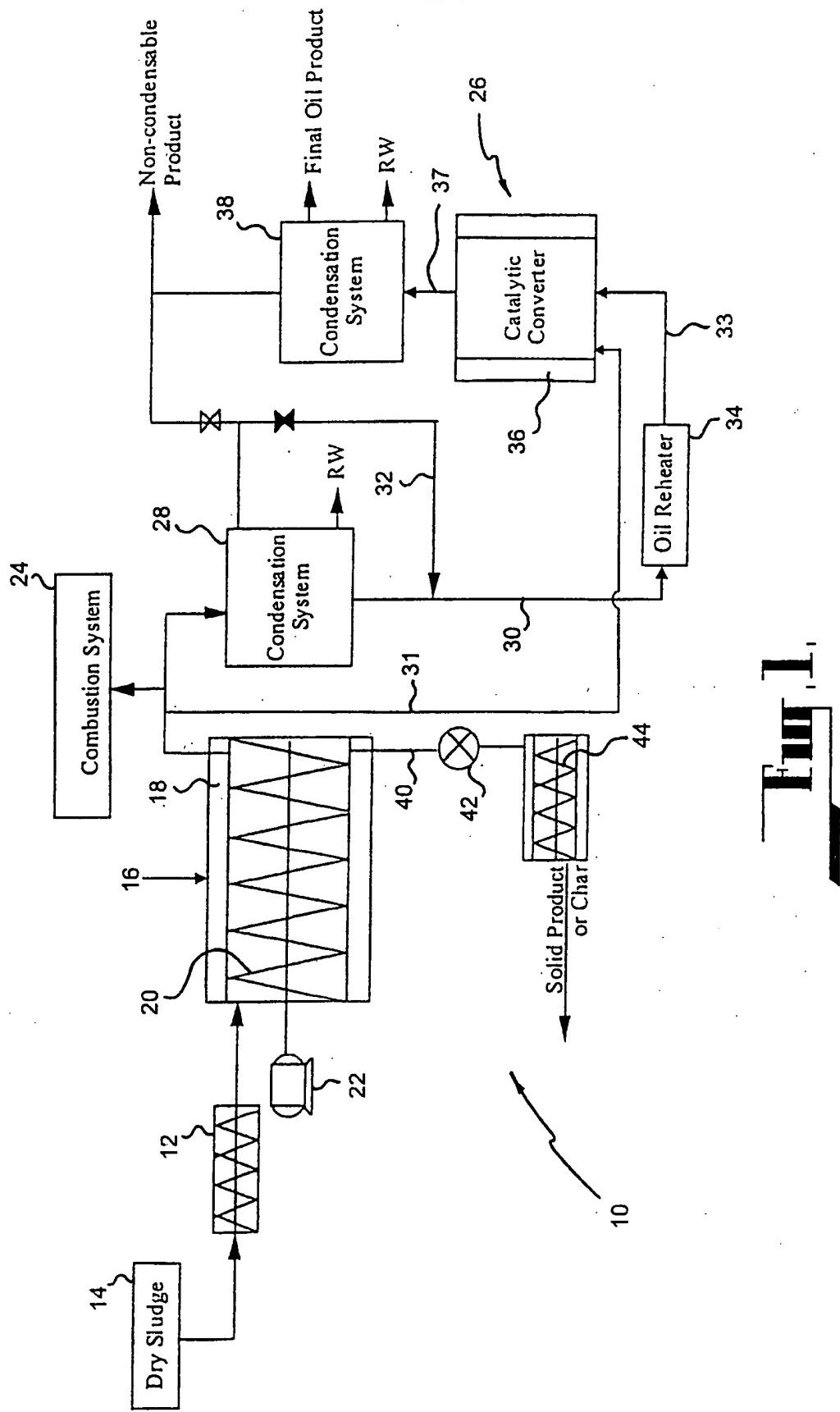
- 24 -

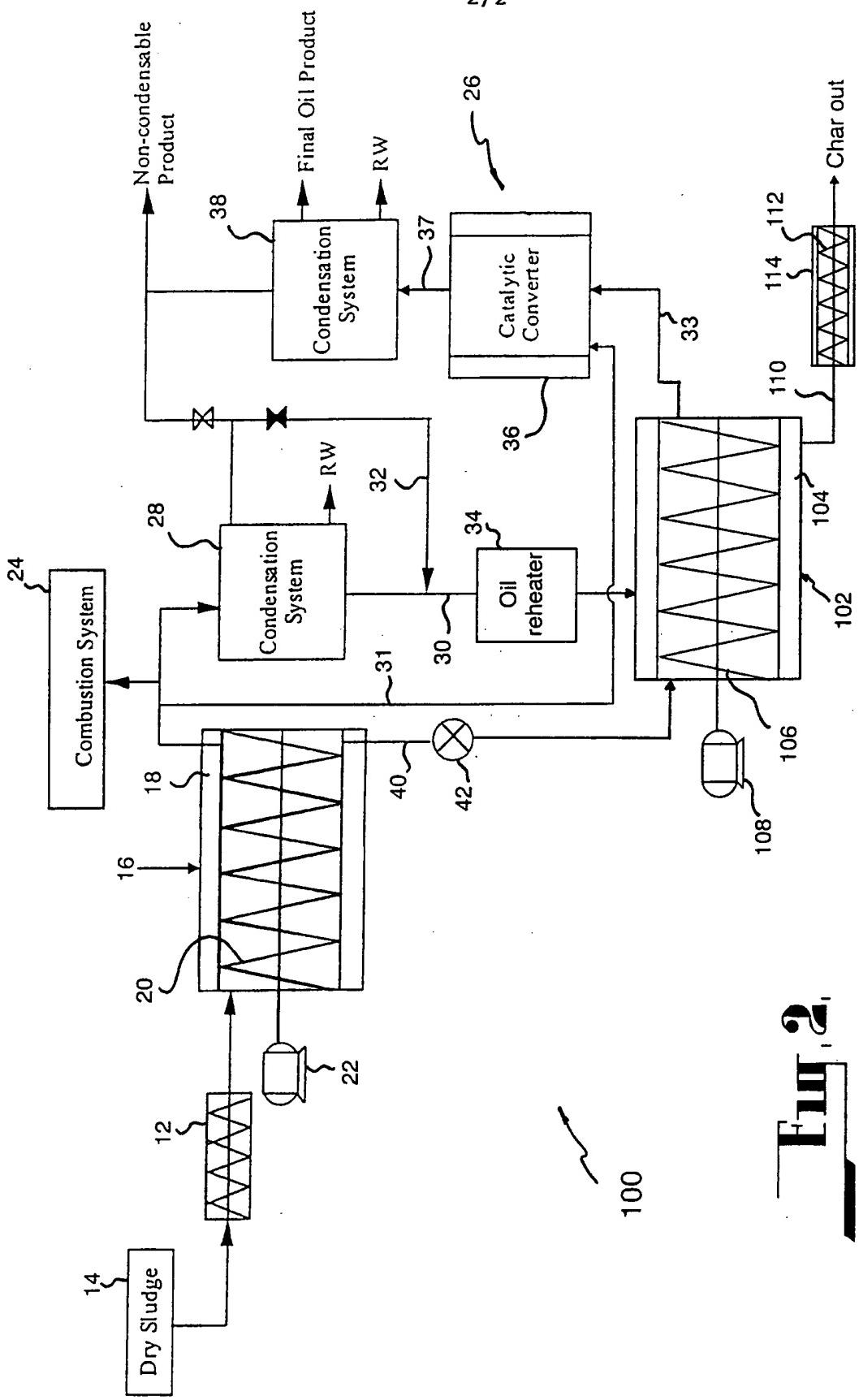
19. A process according to claim 18, wherein the temperature of both reactors is about 450°C.
20. A process according to claim 18, wherein the catalytic converter has a temperature of about 400 to 420°C.
- 5      21. An apparatus for the conversion of carbonaceous materials, the apparatus characterised by a feed system for dried material to be conveyed, a reactor, and a catalytic converter, the reactor having a solid product discharge outlet and a transfer line provided for transport of gaseous product directly or indirectly to the catalytic converter.
- 10     22. An Apparatus according to claim 21, wherein a first condensation system is provided in-line between the reactor and catalytic converter.
23. Apparatus according to claim 22, wherein the first condensation system includes an oil/water separation system.
- 15     24. Apparatus according to any one of claims 21 to 23, wherein the catalytic converter is adapted to contact heated catalyst contained therein with oil or oil and non-condensable products of the condensation system, wherein gaseous products may be removed from the catalytic converter.
- 20     25. Apparatus according to any one of claims 21 to 24, wherein a reheater is provided between the first condensation system and the catalytic converter.
26. Apparatus according to any one of claims 19 to 25, wherein a second condensation system is provided to receive gaseous product from the catalytic converter.
- 25     27. A process for the conversion of sewage sludges substantially as hereinbefore described with reference to Figure 1 or 2.

- 25 -

28. Apparatus for the conversion of sewage sludges substantially as hereinbefore described with reference to Figure 1 or 2.

1/2





## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU 00/00206

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl <sup>7</sup> : C02F 11/10; C10B 53/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) C02F 11/10, 11/00; C10B 53/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT, JAPIO, US (Fulltext) (C02F 11/- or C02C 3/-) plus keywords		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5865956 A (BRIDLE) 2 February 1999 See column 8, lines 44-56, figure 1, abstract	1-28
X	US 5847248 A (BRIDLE) 8 December 1998 See abstract, figure 1 and column 8, lines 24-35	1-28
X	EP 140811 A (CANADIAN PATENTS & DEVELOPMENT) 8 May 1985 See abstract, drawings and page 28	1-28
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C		<input checked="" type="checkbox"/> See patent family annex
<p>* Special categories of cited documents:</p> <p>"A" Document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search 18 April 2000	Date of mailing of the international search report - 9 MAY 2000	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No.: (02) 6285 3929	Authorized officer  <b>JAMES DZIEDZIC</b> Telephone No.: (02) 6283 2495	

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 00/00206

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5114541 A (BAYER) 19 May 1992	
A	DE 3221495 A (LINDE) 8 December 1983	
A	EP 373577 A (STILL OTTO) 20 June 1990	

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/AU 00/00206

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member					
US	5865956	AU	17711/97	CA	2201420	EP	799801		
		JP	10015593	US	5847248				
US	5847248	AU	17711/97	CA	2201420	EP	799801		
		JP	10015593	US	5865956				
EP	140811	CA	1225062	JP	60099399	US	4618735		
		US	4781796	ZA	8407161				
US	5114541	CA	1182062	DE	3042964	EP	52334		
		JP	57111380						
DE	3221495	NONE							
EP	373577	NONE							
END OF ANNEX									

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**